

Name of research institute or organization:

Particle Chemistry Department
Institute for Atmospheric Physics, University of Mainz
and Max Planck Institute for Chemistry, Mainz

Title of project:

Mass spectrometric studies of ice nuclei and background aerosol within CLACE 6

Project leader and team:

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Project description:

The identification of ice nuclei is crucial for the understanding of heterogeneous ice nucleation in supercooled clouds, which is the main initiation process of precipitation in mid latitudes. Until today it is not well understood which chemical components (e.g. sulfuric acid, ammonium, nitrate, various organic substances, mineral dust, sea salt, soot, or other materials) contained inside or on the surface of aerosol particles enable a particle to act as an ice nucleus (IN). While water soluble compounds are expected to favour the formation of liquid cloud droplets, insoluble materials like mineral components may favour the formation of ice particles.

Similar to the 5th and other previous Cloud and Aerosol Characterization Experiments (CLACE-3, CLACE-4, CLACE-5), also in 2007 mass spectrometric measurements of particles were performed at the High Alpine Research Station Jungfraujoch within the frame of the follow-up project CLACE 6. Our CLACE 6 sub-project was embedded into the activities and largely financed by the German Collaborative Research Center SFB 641 "The Tropospheric Ice Phase", sub-project A3 "In situ measurements of the chemical composition of atmospheric ice residuals and ice nuclei by mass spectrometric methods".

During CLACE 6 two different types of aerosol mass spectrometers were operated at the Sphinx laboratory in order to analyze in situ and on-line the chemical composition residuals of supercooled cloud droplets, small ice particles as well as background and interstitial aerosol particles.

The first mass spectrometer, a Time-of-Flight Aerosol Mass Spectrometer (W-ToF-AMS by Aerodyne) is an improved version of the Quadrupole Aerosol Mass Spectrometer that was already deployed to the Jungfraujoch during CLACE 3 and 4. This improved version has a significantly higher sensitivity (only 20 ng/m³ of aerosol mass is needed) and a very high mass resolution of >4000. The mass spectrometer operated very successfully and the chemical composition of the non-refractory compounds of the background and interstitial aerosol (sulfate, nitrate, organics and ammonia) was measured quantitatively throughout the campaign at high time resolution. The high mass resolution allows to distinguish ions of different chemical composition but identical integer m/z ratio: for example, the ions of C₂H₃O⁺ and C₃H₇⁺ at m/z 43.0184 and 43.0551 were clearly separated and this separation allows

to analyze the degree of oxidation of the organic aerosol fraction. The W-ToF-AMS provided successful measurements of ice residuals and background aerosol. An important new finding of these measurements is that the ice residuals did contain a small fraction of organic material, clearly above the instrumental detection limit. This organic material was hardly oxidized but the organic fraction seems to be formed mostly from un-oxidized so-called hydrocarbonlike organic aerosol (HOA).

The second mass spectrometer, a Single Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT), analyzes individual particles in the size range of 300-3000 nm diameter. This mass spectrometer has been developed by our group in recent years and by successfully implementing a number of technical and operational improvements during the last year the sensitivity of the instrument was greatly enhanced. The instrument worked very well and reliable during the campaign and mass spectra for about 10 000 individual background aerosol particles were provided during the campaign. For the first time with this instrument the analysis of individual ice residuals was successfully performed, representing a) a major progress of the technical development of the instrument and b) finally opening up the area of interest for scientific analysis with this instrument.

The SPLAT instrument sampled 25 days with only small interruptions for calibrations and realignment of the particle beam and the laser beams. During that time 9771 background aerosol particles and 357 ice residues were analysed with both polarities. During a one-day experiment 168 CCNs (Cloud Condensation Nuclei) were analysed with the droplet pre-impactor of the Ice-CVI (Ice-Counterflow Virtual Impactor, see report by S. Mertes, IFT Leipzig) being removed. First analysis of some highlights of the data showed that we observed a strong enhancement of lead in the ice nuclei (41.8% of the IN spectra showed a lead signature), while it was present in only 9.1% of the detected background particles and the CCNs exhibited a depletion to 3.7%. Sources for the lead contributions in atmospheric aerosol may include aviation gasoline, smelters, coal combustion, etc. but the influence of lead on cloud formation has not been investigated up to now. Therefore we plan to intensify research and discussion of this topic within the second phase of the SFB-641.

A preliminary result of the SPLAT measurements during CLACE 6 is shown in Figure 4. The spectra from 903 background particles and the spectra from 355 ice residues were processed by a k-means classification algorithm. The pie charts show the percentage of particles (regardless of the particle size) that belong to different groups of particles. It is evident that the IR composition differs strongly from the average background aerosol composition. Mineral dust is by far the dominating

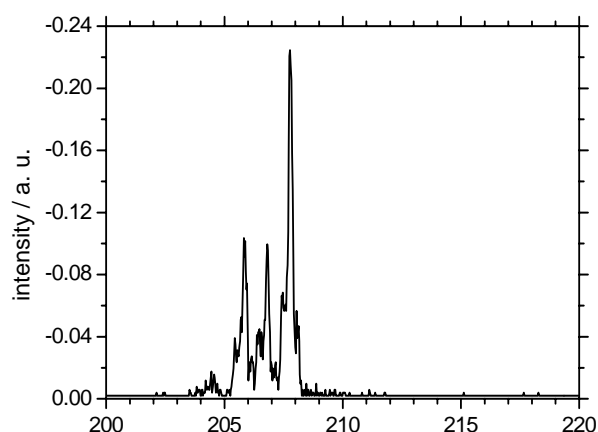
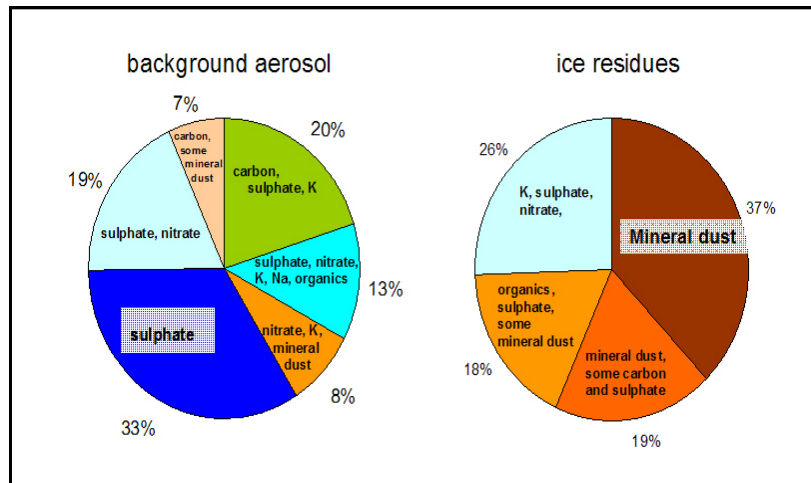


Figure 1: Mass spectrum from a lead containing aerosol particle with the characteristic isotopic pattern at m/z 204, 206, 207 and 208.

substance in the ice residues from fresh ice crystals. The lead in the IR was found in all classes of particles. Further analysis and data interpretation is in progress. The results from the IR measurements with the SPLAT instrument during the CLACE 6 campaign will be presented in a forthcoming paper (Kamphus et al., to be submitted to Atmos. Chem. Phys. Discuss., 2008).



Aerosol composition of the background aerosol and the ice residues from mixed-phase clouds measured with the SPLAT instrument at the Jungfraujoch research station during CLACE 6 in 2007. The IN are clearly dominated by mineral dust. Carbon-containing particles may be soot or organic material. Data are preliminary.

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Key words:

Aerosol chemical composition, ice nuclei chemical composition, aerosol mass spectrometry

Internet data bases:

An FTP server for internal use of CLACE participants has been established

Collaborating partners/networks:

ift Leipzig (Dr. Stephan Mertes), PSI (Dr. Ernest Weingartner), ETH Zürich (Dr. Daniel Cziczo), Tech Univ. Darmstadt (Dr. Martin Ebert),

Scientific publications and public outreach 2007:

Refereed journal articles

Mertes, S., Verheggen, B., Walter, S., Conolly, P., Ebert, M., Schneider, J., Bower, K.N., Cozic, J., Weinbruch, S., Baltensperger, U., and Weingartner, E., 2007: Counterflow virtual impactor based collection of small ice particles in mixed-phase clouds for the physico-chemical characterization of tropospheric ice nuclei: Sampler description and first case study, *Aerosol Science Technology*, 41, 848-864.

Conference papers (for 2007, mostly concerning previous CLACE campaigns)

Kamphus M.; Ettner-Mahl, M.; Drewnick, F.; Curtius, J.; Mertes, S.; Borrmann, S., Chemical analysis of ambient aerosol particles and ice nuclei in mixed phase clouds by single particle laser ablation mass spectrometry, EGU, Vienna, Austria, Geophysical Research abstracts Vol. 9, 06109, 2007.

Schneider J; Walter, S; Curtius, J; Drewnick, F; Borrmann, S; Mertes, S; Weingartner, E; Gysel, M; Cozic, J, In-situ analysis of free tropospheric aerosol and small ice crystal residuals using a High Resolution Aerosol Mass Spectrometer (HR-ToF-AMS) at the Jungfraujoch during CLACE 5, European Aerosol Conference, Salzburg, 2007.

Schneider J; Walter, S; Curtius, J; Drewnick, F; Borrmann, S; Mertes, S; Weingartner, E; Gysel, M; Cozic, J, In-situ analysis of free tropospheric aerosol and small ice crystal residuals using a high resolution aerosol mass spectrometer (HR-ToF-AMS) at Jungfraujoch during CLACE 5, EGU General Assembly, Vienna, Austria, 2007.

Weingartner, E., Verheggen, B., Lohmann, U., Cozic, J., Gysel, M., Baltensperger, U., Mertes, S., Bower, K. N., Connolly, P., Flynn, M., Crozier, J., Gallagher, M., Coe, H., Walter, S., Schneider, J., Curtius, J., Borrmann, S., Petzold, A., Ebert, M., Worringer, A., and Weinbruch, S.: Aerosol Partitioning in Mixed-Phase Clouds, EGU Wien, 2007.

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<http://www.sfb641.uni-frankfurt.de/index.html>

